# Supporting information for: Understanding the dipole moment of liquid water from a self-attractive Hartree decomposition

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# AIMD oxygen-oxygen radial distribution function

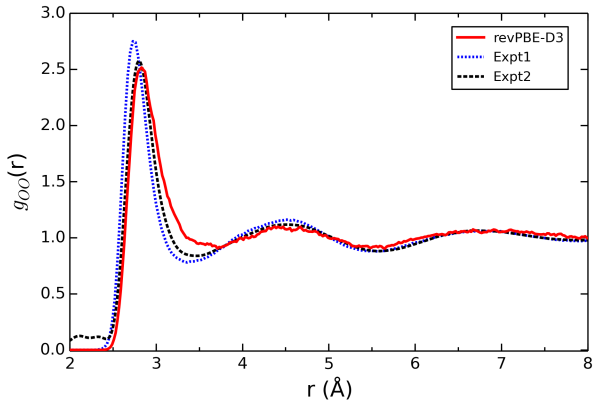


Figure S1: Oxygen-oxygen radial distribution function $g_{\mathrm{OO}}(r)$ of liquid water computed from the AIMD simulation using the revPBE-D3 functional, compared to experimental results. "Expt1" is taken from Ref.,[1] and "Expt2" is taken from Ref.[2]

# SAH density decomposition error analysis

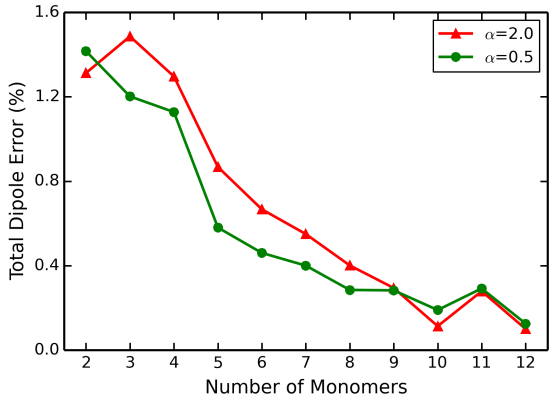


Figure S2: Numerical (percentage) errors of the total dipole moment of water clusters from the SAH decomposition with respect to the input density, using two localization parameters ($\alpha = 0.5$ and $\alpha = 2$), with increasing number of total water molecules, The water cluster geometries are the same as in Fig. 2 of the main text.

The SAH decomposition is a density partition scheme, where the SAH pair densities are constrained to sum to the input total density. Thus, in theory, the dipole of the full system

is exactly sums of the dipoles of the pair densities. In practice, because we implemented the SAH decomposition in finite Gaussian basis, the density constraints are satisfied subject to numerical errors. In Fig. S2, we demonstrate the numerical errors of the total dipole moment of water clusters computed from the SAH decomposition, with increasing number of total water molecules. One can see that even the largest percentage errors are within 1.6%. The errors decrease with increasing number of total water molecules, possibly due to more auxiliary Gaussian basis functions that better constrain the density decomposition. As our main conclusions are drawn from water decamer structures, the expected numerical errors on total dipole moments are below 0.4%.

## Dipole moment distributions of all water molecules in sampled water decamers

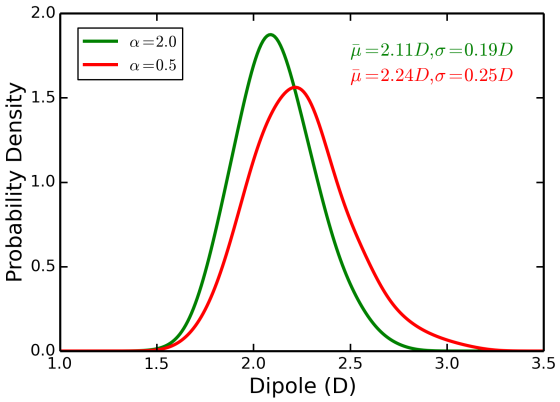


Figure S3: Distributions of the dipole moment of all water molecules in 100 water decamer geometries sampled from the AIMD trajectory, calculated using two localization parameters ($\alpha = 0.5$ and 2) in the SAH decomposition.

In Fig. S3, we show the distributions of the dipole moment of all water molecules in 100 water decamers sampled from the AIMD trajectory, which are the same structures used in Fig. 3 of the main text. We find the same trend as in Fig. 3, i.e., the more localized decomposition yields smaller average dipole moment and polarizability. However, the differ-

ence between the two distributions are not as obvious as in Fig. 3, where only the central water molecule is considered. This is because the "edge" water molecules are not fully surrounded by other water molecules, and are less polarized and have smaller degree of charge delocalization.

## Numerical test of dependence on basis sets

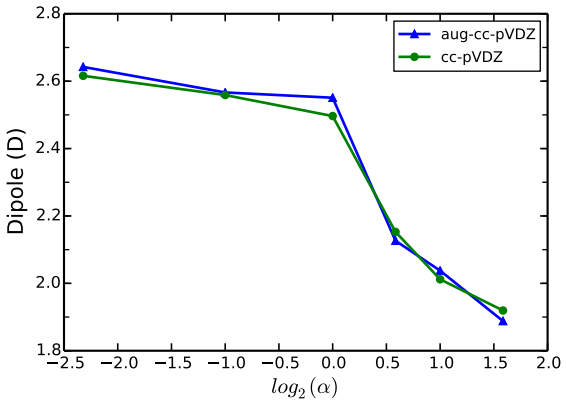


Figure S4: Dipole moment of a water monomer in the water tetramer from the SAH decomposition, using the uncontracted aug-cc-pVDZ and cc-pVDZ basis sets.

Since the SAH decomposition is a density partitioning scheme, it does not suffer from numerical instability due to diffuse basis functions like localized molecular orbital methods. To confirm this point, we perform SAH decomposition for the water tetramer in the uncontracted cc-pVDZ basis, and compare the dipole moment results to the uncontracted aug-cc-pVDZ basis, as shown in Fig. S4. The cc-pVDZ results follow the same trend as the aug-cc-pVDZ results, and the dipole moment difference between the two basis sets is within 0.05 D. Therefore, the results in this paper do not depend on the augmentation of basis function.

# References

(1) Soper, A. K. The radial distribution functions of water and ice from 220 to 673 K and at pressures up to 400 MPa. *Chem. Phys.* **2000**, *258*, 121–137.

(2) Skinner, L. B.; Huang, C.; Schlesinger, D.; Pettersson, L. G.; Nilsson, A.; Benmore, C. J. Benchmark oxygen-oxygen pair-distribution function of ambient water from x-ray diffraction measurements with a wide Q-range. *J. Chem. Phys.* **2013**, *138*, 074506.